

## PATENT COOPERATION TREATY


## PCT

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference JDMAP203202WO	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/GB 03/05565	International filing date (day/month/year) 18.12.2003	Priority date (day/month/year) 20.12.2002
International Patent Classification (IPC) or both national classification and IPC C01B21/06		
Applicant UNIVERSITY OF NOTTINGHAM et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 6 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the opinion</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input type="checkbox"/> Certain observations on the international application</p>		
Date of submission of the demand  19.07.2004	Date of completion of this report  28.06.2005	
Name and mailing address of the International preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tlx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer  Zalm, W  Telephone No. +31 70 340-2804	



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB 03/05565

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

1, 2, 4, 6, 7 as originally filed  
3, 3a, 5, 8, 9 received on 25.10.2004 with letter of 19.10.2004

**Claims, Numbers**

1-9 as originally filed  
10-16 received on 25.10.2004 with letter of 19.10.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

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6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	5,6
	No: Claims	1-4,7-16
Inventive step (IS)	Yes: Claims	5,6
	No: Claims	1-4,7-16
Industrial applicability (IA)	Yes: Claims	1-16
	No: Claims	

2. Citations and explanations

**see separate sheet**

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability:  
citations and explanations supporting such statement**

(i) Reference is made to the following documents:

D1: US 6 398 125 B1 (JANG BOR ZENG ET AL)

D2: US 4 234 554 A (MUELLER GERTRAUDE ET AL)

D3: US 2 488 054 A (DAVIS LEWIS W)

(ii) The application does not meet the requirements of Article 6 PCT because **claims 1-16** are not clear.

(a) The expression 'nanoscale structure' is vague and not defining a technical feature as required by Rule 6.3(a) PCT: 'nanoscale' is vague without specification of a range of the property to which it should refer (e.g. 1-100 nm) and 'structure' is not a feature defining an entity but deals with an extensive property (like crystal structure) including an unlimited number of (undefined) possibilities.

It appears that the objective can be overcome in case expression 'anisotropic nanoscale structure' is replaced either by 'particles having a size in the nanometer range and being anisotropic in morphology' or by incorporation of the features of claim 5 in the **independent claims 1, 12 and 14** in order to come to a definition according to the requirements of the PCT.

(b) The subject-matter of claims 1, 13 and 14 includes anisotropic particles on nanometer scale of a extensive number of compositions: (at least) one of the elements combined of group IA (alkali metal) or IIA (alkaline earth metals) combined with (at least) one of the elements of group IIIA (borides, etc), IVA (carbides, silicides, etc.) and VA (nitrides, phosphides, etc.). In the description of the application under consideration only the preparation of Li<sub>3</sub>N with the defined particle features is described. The scope of the independent product claim 1 and of the independent process claims 13 and 14 however is not such that it refers to Li<sub>3</sub>N only. The compounds other than Li<sub>3</sub>N are considered not supported by the description and these claims thus do not meet the requirement of Article 6 PCT.

Moreover from the method of preparation (claim 14-16) there is serious technological doubt whether the use of other gases than nitrogen results in the materials with different anions (carbides and borides) and with the particle size and morphology as defined in claim 1. I

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appears that based on the single example given in the description the preparation of other alkali metal nitrides in addition to that of lithium with the specified particle properties can be expected. Independent claims dealing with 'alkali metal nitrides' are considered to meet Article 6 PCT.

(iii) The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of **claims 1-4 and 7-16** in its present definition is not new in the sense of Article 33(2) PCT.

Document D1 (US 6 398 125 B1 (JANG BOR ZENG ET AL) 4 June 2002) discloses a process for the preparation of nanosized nitrides whereby liquid metal or alloy powders are produced and reacted in a nitrogen containing atmosphere. One of the low melting point metals which can be used is lithium (see claims 6,9). The preparation of carbides, borides is also mentioned. The subject-matter of claims 1-4 and 7-16 of the present application (not limited to 'anisotropic nanostructures' properly redefined as indicated under item (ii) above) is thus not new. The document specifies also several uses of the material. Use claim 13 is regarded to lack novelty too.

D2 (US 4 234 554 A (MUELLER GERTRAUDE ET AL) 18 November 1980) teaches the preparation of lithium nitride by heating lithium in a closed container with nitrogen e.g. at a pressure below 100 kPa (claim 4: >250 mmHg). In claim 14 the specification 'for the production of .....claim 1-12' is not a limiting feature further defining the invention. Document D2 (although it does not teach the preparation of materials having nanometer-sized particles) therefore is novelty destroying for the process of claims 14 and 15.

In a similar way is a novelty objection to be based on D3 (US 2 488 054 A (DAVIS LEWIS W) 15 November 1949) wherein the preparation of magnesium nitride from metallic magnesium and a gaseous nitrogen source at low temperature and at low (partial) nitrogen pressure is described.

WO98/24576A discloses "nanostructured" metals, alloys and carbides but these are again approx isotropic nanoparticles of <100 nm diameter.

US5876682 discloses nanostructured nitride ceramic powders of <1000 nm and again these are essentially isotropic materials.

CN1348919A discloses nanosized titanium carbide but again these are nanoparticles and this patent only discloses a single material. Similarly, CN1371863 discloses nanosized titanium boride and again the material is in the form of nanoparticles. This patent also only covers one example.

US5997832 discloses nanorods of metal carbides with diameters <100 nm and aspect ratios of 10-1000 and WO96/30570A discloses nanofibrils of carbides of any metal but in each case there is no disclosure of any nanotube type structure.

US6398125 discloses a process for the preparation of nanosized nitrides comprising heating a molten metal to an ultra-high temperature and atomizing the melt into fine liquid droplets. The stream of droplets is then introduced into a second-stage atomizer chamber and further atomized. The nanometer-sized droplets are then cooled and collected as solid particles.

US42344554 discloses a process for the preparation of lithium nitride by heating lithium in a closed container with nitrogen at a pressure below 100 k pa.

However, the prior art does not disclose any form of nanotube based either entirely or predominantly on material other than carbon or indeed any anisotropic nanostructures based on Group IA metals. The interest in carbon nanotubes arises because of the possibility of allowing step changes in the performance of a wide range of systems. However, the number of applications of carbon nanotubes is limited by the range of structures and electronic properties available. The present invention aims to provide a wide range of nanoscale structures such as nanorods, nanofibres and nanotubes from

materials other than carbon. It is also within the scope of the invention to produce nanoscale structures which incorporate carbon but which would not be classified as carbon nanostructures because of their low (ie less than 50% carbon content).

According to one aspect of the present invention there is provided an anisotropic nanoscale structure formed from at least one element selected from groups IA and IIA of the periodic table and at least one element selected from groups IIIA, IVA, and VA.

In an embodiment, the nanostructure is inorganic.

nanostucture either to produce a non-stoichiometric structure containing lithium, nitrogen and oxygen or to produce a nanostucture effectively based on lithium oxide.

In another aspect of the present invention, there is provided a process for the production of a nanostucture as defined previously, the process comprising exposing the metal of Group IA or IIA to a gaseous source of the element of Group IIIA, IVA, or VA, optionally in the presence of a transition metal, in a sealed heated chamber at a pressure between atmospheric pressure and a pressure of  $10^{-2}$  Pa ( $10^{-4}$  torr), wherein the upper limit of the temperature is not more than 1200°C.

Preferably, in the process the upper limit of the temperature is defined by the temperature of decomposition of the compound.

In an embodiment, the process is used to make lithium nitride. In this case, lithium is heated in the presence of nitrogen in a sealed vessel until the pressure in the vessel is constant to form a lithium nitride nanostucture.

Inorganic nanostuctures, such as those based on lithium nitride are expected to be of benefit in a number of applications on account of the number of different properties which are available from materials of this type. Thus, for example lithium nitride is a superionic conductor and nanostuctures derived from lithium nitride therefore are likely to find application in materials such as rechargeable nano-batteries and other electronic components. This is one application for which carbon nanostuctures are clearly unsuitable.

The anisotropic structures of the present invention, including but not limited to rods, fibres, tubes, have a number of applications on account of their properties.

Thus the nanostuctures of the present invention have a number of applications such as: ionic conductors/battery components, in hydrogen storage devices, for templating nanowires, electrical devices, catalysis and synthesis, flat screen technology (display



should be at least twice its diameter in order to ensure a favourable temperature gradient. Temperature gradients are particularly important in chemical vapour transport techniques for producing inorganic nanostructures such as those of the chalcogenides.

We have also found that the product only forms if the pressure is reduced below atmospheric pressure. However, we have also found that it is still necessary for there to be a certain amount of gas present in the reactor vessel and it is believed that this behaves as a transport gas. There is, however, a lower limit to the pressure in the reaction vessel and we have found that the synthesis does not progress well below a pressure of  $10^{-2}$  Pa ( $10^{-4}$  torr). The upper limit of the acceptable pressure range is atmospheric pressure.

It is also important that the temperature is sufficiently high that the inorganic compound becomes volatile. In the case of lithium nitride a suitable temperature range is between  $150^{\circ}\text{C}$  and  $300^{\circ}\text{C}$  depending on the pressure in the reaction vessel. The upper limit of the temperature is governed by the need to avoid decomposition of the inorganic compound, although some decomposition may be tolerated as it is believed that the individual elements may be transported and recombined in the vapour phase in certain inorganic compounds.

The presence of a transition metal in the reaction vessel during the formation of certain inorganic compounds has been found to be beneficial in producing the nanostructure or to alter the nature of the nanostructure. Thus, in the case of lithium nitride, the presence of ~~iron~~ powder in the reaction vessel leads to an alteration in the manner in which the sheets roll up. Thus, the presence of a transition metal may have a catalytic and/or structure directing effect in the formation of an inorganic nanostructure. In addition, there is the ~~possibility~~ of integrating (substituting) the transition metal into the walls of the inorganic nanostructure.

The present invention will now be illustrated with reference to the example of the ~~preparation~~ of an inorganic nanostructure based on lithium nitride. Lithium nitride can be formed by exposing lithium metal to nitrogen gas at room temperature. Alternatively,

lithium can be heated in the presence of nitrogen. Lithium nitride can also be produced by using molten sodium as a solvent for lithium which is then reacted with nitrogen.

The dissolution of lithium in sodium is carried out in an argon-filled glove box and the sodium is kept molten using a hot plate to provide heating. The molten sodium keeps the argon atmosphere clean by reacting with any residual oxygen gas or water vapour which may be present. The lithium is dissolved in the molten sodium and the crucible containing the mixture is then removed from the hot plate and allowed to cool. Once cool, the crucible is sealed in a reaction vessel in a furnace again in an argon gas atmosphere and heat and nitrogen are supplied. A clump of red fibrous material, consisting of lithium nitride nanotubes, grows above the crucible on a convenient surface provided within the furnace. Suitable surfaces include, for example, a loop of iron wire. The argon gas atmosphere is removed using a suitable pump and is replaced with nitrogen which is introduced under a positive pressure (typically 1.5 atmospheres). The reactants are heated to between 400 and 500°C, preferably about 460°C, for up to 72 hours and the pressure in the reaction vessel is monitored with a pressure transducer to measure pressure changes during the reaction. After a suitable period of time, usually between 6 and 72 hours, the reaction is complete and the point of completion can be measured by the pressure transducer. The pressure in the reaction vessel is constant once the reaction is complete and the vessel is then quenched to room temperature.

The reaction vessel includes a cold finger into which water is then placed and the vessel evacuated to a pressure of  $10^{-2}$  Pa ( $10^{-4}$  torr) or less. The vessel is again heated to between 400 and 500°C, preferably about 450°C, for up to 24 hours under a dynamic vacuum in order to distill off the sodium which recondenses on the cold finger. Lithium nitride in the form of a purple crystalline product remains in the crucible and may be collected.

10. A nanoscale structure as claimed in any preceding claim, wherein the nanostructure is a nanotube in which the hollow core has been filled with a metal to form a metallic nanowire.

11. A nanoscale structure as claimed in any preceding claim, wherein chemical modification of the nanostructure has been performed in order to enhance or tailor the properties of the nanostructure.

12. An anisotropic nanoscale structure based on lithium nitride ( $\text{Li}_3\text{N}$ ).

13. Use of an anisotropic nanostructure according to any of claims 1 to 12 in an ionic conductor/battery component, a hydrogen storage device, for templating nanowires, an electrical device, catalysis, a flat display screen, or as a structural member.

14. A process for the production of a nanostructure as defined in any of claims 1 to 12, the process comprising exposing the metal of Group IA or IIA to a gaseous source of the element of Group IIIA, IVA, or VA, optionally in the presence of a transition metal, in a sealed heated chamber at a pressure between atmospheric pressure and a pressure of  $10^{-2}$  Pa ( $10^{-4}$  torr), wherein the upper limit of the temperature is not more than  $1200^\circ\text{C}$  and wherein said chamber comprises a cold finger into which water is placed.

15. A process as claimed in claim 14, wherein the upper limit of the temperature is defined by the temperature of decomposition of the compound.

16. A process as claimed in claim 14 or 15, wherein lithium is heated in the presence of ~~nitrogen~~ in a sealed vessel until the pressure in the vessel is constant to form a lithium ~~nitride~~ nanostructure.